

CLASSIFICATION RESTRICTED
 SECURITY INFORMATION
 CENTRAL INTELLIGENCE AGENCY
 INFORMATION FROM
 FOREIGN DOCUMENTS OR RADIO BROADCASTS

50X1-HUM

REPORT

CD NO.

COUNTRY USSR

DATE OF
INFORMATION 1951

SUBJECT Scientific - Chemistry

DATE DIST. 23 Apr 1952

HOW
PUBLISHED Trimonthly periodical

NO. OF PAGES 4

WHERE
PUBLISHED MoscowDATE
PUBLISHED 21 Nov 1951SUPPLEMENT TO
REPORT NO.

LANGUAGE Russian

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE
 OF THE UNITED STATES WITHIN THE MEANINGS OF ESPIONAGE ACT 50
 U. S. C. 31 AND 32 AS AMENDED. ITS TRANSMISSION OR THE REVELATION
 OF ITS CONTENTS IS A VIOLATION OF THE LAWS OF THE UNITED STATES
 AND IS PROHIBITED BY LAW. REPRODUCTION OF THIS FORM IS PROHIBITED

THIS IS UNEVALUATED INFORMATION

SOURCE Doklady Akademii Nauk SSSR, Vol LXXXI, No 3, 1951, pp 427-430.

METHOD OF PARAMAGNETIC RESONANCE ABSORPTION
IN THE MAGNETOCHEMISTRY OF ORGANIC COMPOUNDS

B. M. Kozyrev
 Phys Tech Inst
 Kazan' Affiliate, Acad Sci USSR

In organic chemistry, determinations of statistical magnetic susceptibility are of importance in investigating free radicals and biradicals, which have unpaired electrons.

Extension of magnetochemical methods of investigation to other classes of substances meets with the following obstacle: the measurable static susceptibility usually represents an algebraic sum of the diamagnetic and paramagnetic components. Separation of these components or parts by a direct experimental procedure is impossible within the framework of static methods. In the case of strongly paramagnetic substances, the diamagnetic component of the susceptibility amounts to a small correction only, so that an approximate estimate of its value is sufficient. In the case of diamagnetic substances, however, the paramagnetic component of susceptibility may be large in comparison with the diamagnetic part.

In the empirical system of Pascal magnetic increments, a positive (paramagnetic) increment must be assigned to a number of structural elements, particularly the double bond, the conjugated double bond, the triple bond, etc. At the same time, it is impossible to establish the nature of the correction involved. To a structural paramagnetic increment may correspond (a) simple reduction of diamagnetism due to modification of atomic configuration as a result of a change in the type of the bond; (b) paramagnetism which is independent of the temperature; and (c) normal paramagnetism of the type observed in free radicals. It is very difficult to separate these three effects from each other in every individual case to distinguish between them.

- 1 -

CLASSIFICATION RESTRICTED

STATE	<input checked="" type="checkbox"/> NAVY	<input checked="" type="checkbox"/> NSRB	DISTRIBUTION																
ARMY	<input checked="" type="checkbox"/> AIR	<input checked="" type="checkbox"/> FBI	<u>AEC</u>	<input checked="" type="checkbox"/>															

50X1-HUM

RESTRICTED

The method of paramagnetic resonance brings considerable improvement to the situation. Resonance absorption of energy from a magnetic field of radio frequency is a purely paramagnetic effect. For that reason, with its aid, true paramagnetism of a substance can be separated in cases where it is usually masked by diamagnetism in static measurements.

Originally, the method of paramagnetic resonance was applied by the author and S. G. Salikhov (1), who obtained curves of resonance absorption for the free radical $C_{35}H_{25}$ (pentaphenylcyclopentadienyl). The curve of absorption in the case of this substance has a single resonance peak, the position of which corresponds to the gyromagnetic factor $g \approx 2$. This indicates the pure spin character of the magnetism of $C_{35}H_{25}$ molecules and permits the conclusion that the ground state of these molecules is the Σ -state. Measurements of the static susceptibility of $C_{35}H_{25}$ in a broad temperature range lead to the same conclusion (2).

Thanks to improvement in the sensitivity of the apparatus, it became possible, at present, to begin investigation of paramagnetic resonance in the case of diamagnetic substances.

Experimentally paramagnetic resonance is investigated by determining the dependence of the coefficient of paramagnetic absorption X (or of the high-frequency susceptibility χ') on the intensity of the static magnetic field H , disposed perpendicularly to a magnetic field of constant amplitude $H_0 \ll H$ and constant frequency ν . A necessary condition of resonance is coincidence of this frequency with the frequency of Larmor's precession to which the kind of particles investigated (atoms, molecules, or ions) is subjected in the external field H :

$$\nu = (g\beta/h) H$$

Here, h is Planck's constant, β Bohr's magneton, and H the intensity of the static field H which corresponds to the maximum of X . The values of X were measured in our experiments at the frequency $\nu = 2.17 \times 10^8$ Hertz [cycles] by use of a network-current method proposed by Ye. K. Zavoyskiy (4) and were expressed in relative units.

Several substances were investigated in which the presence of disguised paramagnetism could be suspected. These included anthracene, allocymene $\begin{matrix} CH_3 \\ \diagup \\ C=CH-CH=CH-C=CH-CH_3 \end{matrix}$, 1,9-bis-(2-furyl)-5-oxo-1,3,6,8-nonatetraene ($C_{17}H_{14}O_3$), and 1,9-diphenyl-5-oxo-1,3,6,8-nonatetraene ($C_{21}H_{18}O$).

It is known that anthracene exhibits a strong exaltation of the refraction and an abnormally low diamagnetism, as far as Pascal increments are concerned. Allocymene contains three conjugated double bonds, while the molecules $C_{17}H_{14}O_3$ and $C_{21}H_{18}O$ are examples of highly conjugated systems (they contain 9 and 10 conjugated double bonds, respectively, considering that the bonds of the cyclic groups and of the $C=O$ group also participate in the conjugation). Experiments with benzene and furfural were carried out for control purposes. In the case of benzene, there is no reason for expecting any hidden paramagnetism. One may make the same assumption in regard to furfural, although with less certainty.

RESTRICTED

50X1-HUM

RESTRICTED

The results may be summarized as follows:

1. No paramagnetic absorption has been detected in either benzene or furfural.
2. A measurable effect of this type has been detected in the cases of anthracene and allocymene. The curve $\chi''(H)$ has a single resonance peak corresponding to an effective gyromagnetic factor $g \approx 1$. When the temperature is reduced by more than a factor of 3 (from 300 to 90°K), the intensity at the peak increases in the case of anthracene by ~15% and in the case of allocymene by ~25%. Consequently, we are dealing with paramagnetism which does not depend strongly on the temperature. The data for allocymene are shown in Figure 1 (appended).
3. The most interesting results were obtained on $C_{17}H_{14}O_3$ and $C_{21}H_{18}O$. At 300°K each of these substances yielded $\chi''(H)$ curves with two resonance peaks of approximately the same intensity. One of them corresponds to the pure spin value of the gyromagnetic factor, i. e., $g \approx 2$, while the other corresponds to $g \approx 1$. On cooling to 90°K, the first peak is reduced to such an extent that it practically disappears against the background of the second peak, whose intensity grows by approximately 30%. The results for $C_{17}O_{14}O_3$ are shown in Figure 2 (appended).

Here, we apparently have two different causes of the effect: (a) paramagnetism of the type observed by us in anthracene and allocymene; and (b) normal paramagnetism of the type exhibited by free radicals. Normal paramagnetism must increase on cooling (at a rate which is inversely proportional to the absolute temperature). However, the probability of the existence of excited states of the free radical type becomes very small on cooling to the temperature of liquid oxygen. This explains the disappearance of the resonance peak.

The results outlined above permit the following conclusions:

1. Excited states of the free radical type are absent in benzene and furfural.
2. Such states are apparently also absent in anthracene and allocymene. However, these substances exhibit paramagnetism the origin of which has not yet been clarified. This paramagnetism is difficult to explain by the presence of paramagnetic impurities in our samples (cf. the unusual value of the g factor and the low degree of temperature dependence).
3. In the highly conjugated compounds $C_{17}O_{14}O_3$ and $C_{21}H_{18}O$, excited states of the free radical type are present at room temperature. They practically disappear at the temperature of liquid oxygen. The fact that the probability of such states increases with the increase in the number of double bonds in the molecule (as comparison with allocymene shows) may be related to the increased stability of free radicals, which also depends on the increase of the number of double bonds.

As far as we know, the experiments described above represent the first direct experimental proof of the existence of hidden paramagnetism in diamagnetic substances. The results obtained in these experiments permit conclusions which are of importance from the viewpoint of the theory of the chemical bond. The low intensity of the absorption lines precludes a strictly quantitative comparison with data on static susceptibility at this stage. Nevertheless, the order of magnitude of the observed effects is in agreement with the values which may be expected on the basis of Pascal increments.

- 3 -

RESTRICTED

50X1-HUM

RESTRICTED

The author wishes to thank B. A. Arbuzov, corresponding member, Academy of Sciences USSR for his interest in the investigation and for supplying the substances which were investigated. Thanks are also due to S. G. Salikhov and N. S. Garif'yanov for their collaboration.

BIBLIOGRAPHY

1. B. M. Kozyrev, S. G. Salikhov, DAN SSSR, Vol LVIII, p 1023, 1947
2. E. Mueller, J. Mueller-Rodolff, Berichte, Vol LXVIII, No 4, p 785, 1936
3. L. Enderlein, Annales de Chimie, Vol X, 5, 1938
4. Ye. K. Zavoytsky, Doctor's Dissertation, Institute of Physics, Academy of Sciences USSR, 1944

X
[Appended figures follows.]

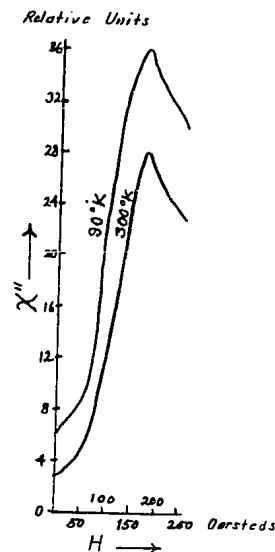


Figure 1. $\chi''(H)$ Curves of Allocymene

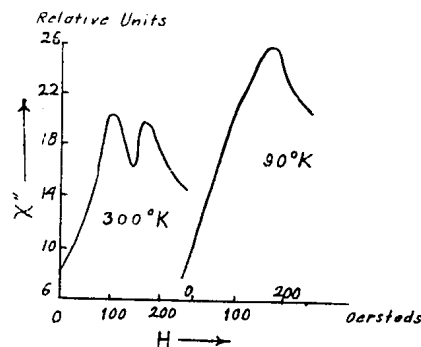


Figure 2. $\chi''(H)$ Curves of $C_{17}H_{14}O_3$ and $C_{21}H_{18}O$

- E N D -

- 4 -

RESTRICTED